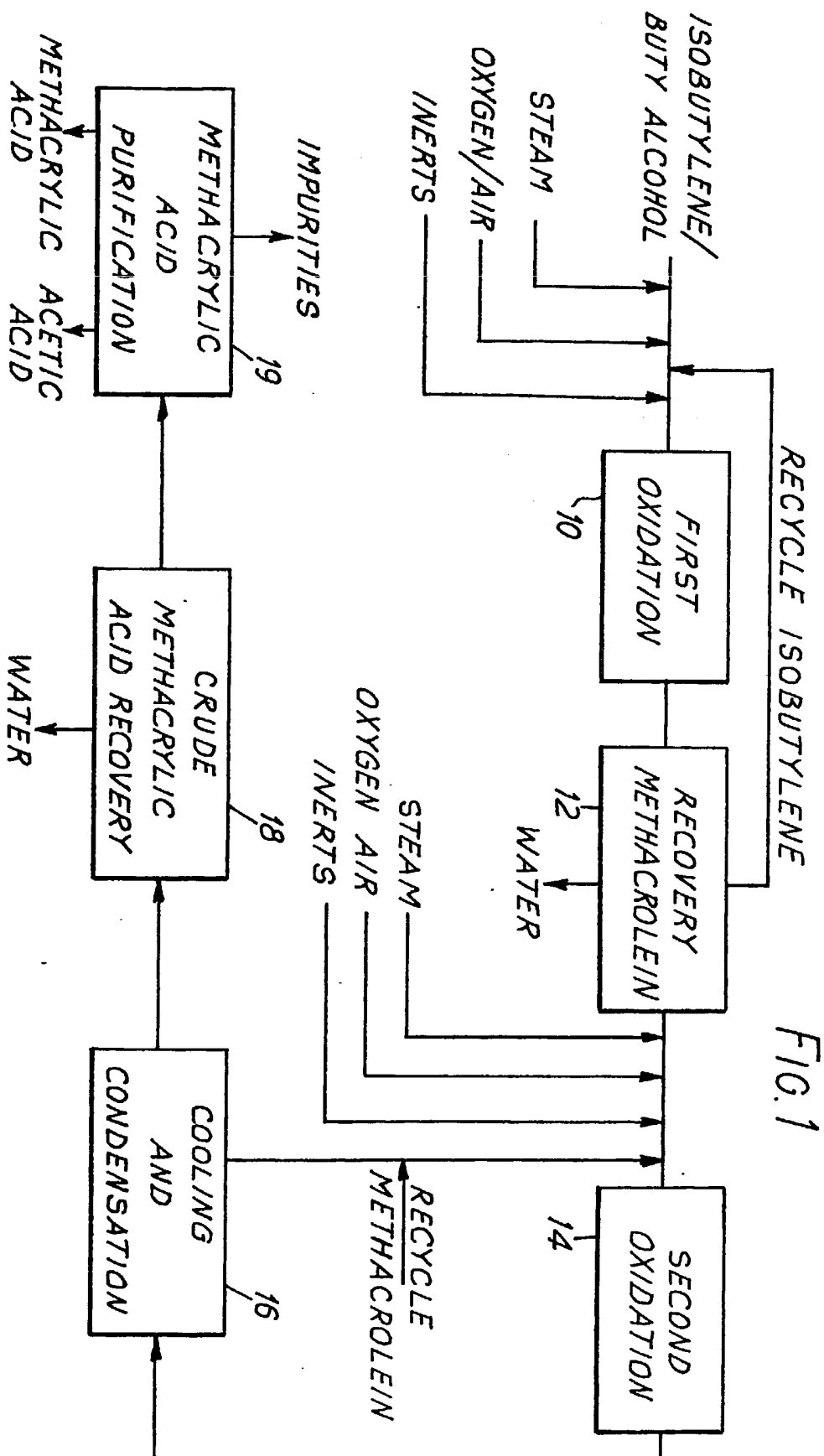

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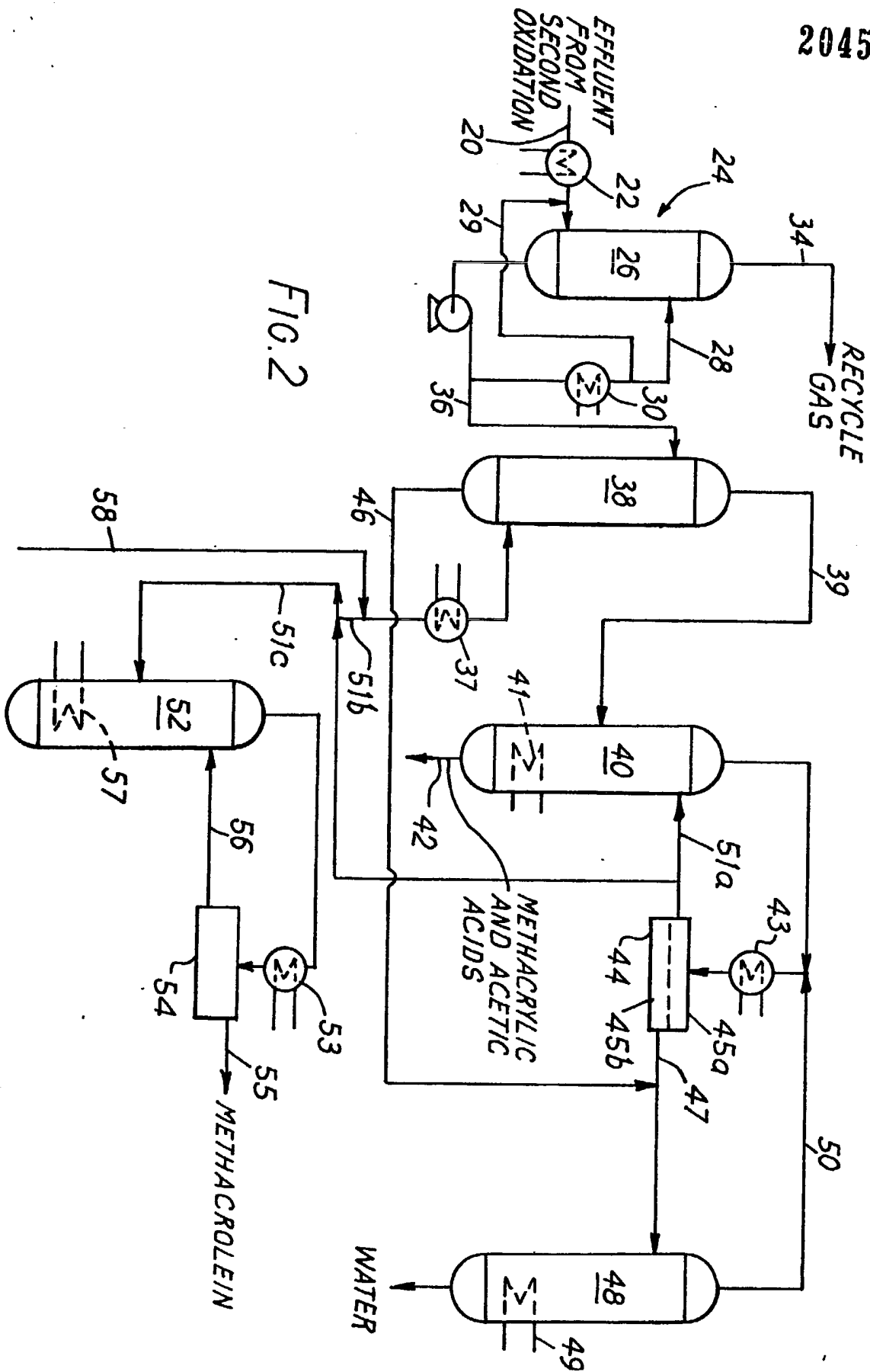
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**(54) Process for recovering
methacrylic acid**

(57) In an oxidation process for converting methacrolein to methacrylic acid, the product methacrylic acid is recovered by cooling and condensing the effluent from the oxidation. The condensed effluent, which contains methacrylic acid and water as the major components along with by-product acetic acid, a minor amount of unreacted methacrolein and impurities, is extracted with a suitable solvent, preferably a ketone-aromatic mixture, most preferably a methyl n-propyl ketone-toluene mixture in order to reject water and impurities. Substantially dry crude methacrylic acid including by-product acetic acid is separated from the solvent by distillation of the rich solvent. Water and the solvent are taken overhead, condensed and separated as solvent-rich and water-rich phases. The recovered solvent is returned to the extraction column. A portion of the solvent-rich phase is distilled to recover methacrolein, while the water-rich phase is sent to a stripping column for recovery of residual solvent. Water is withdrawn from the bottom of the stripping column and reused or discarded, as desired.

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SPECIFICATION

Process for recovering methacrylic acid

- 5 The present invention relates in general to processes for production of methacrylic acid from methacrolein by oxidation. In particular, the invention relates to a two-step oxidation process in which a feed stock comprises isobutylene and/or tertiary butyl alcohol is oxidized first to methacrolein and thereafter to methacrylic acid, with both steps being carried out at a temperature in the range of 270-500°C in the presence of molecular oxygen over a catalyst. Such processes are known generally in the art. An example is U.S. 4,087,382, disclosing a process and a catalyst for the production of methacrolein from isobutylene and/or tertiary butyl alcohol. The second step in which the methacrolein is oxidized to methacrylic acid is disclosed in U.S. 4,001,316. 5
- 10 In addition to the two-step oxidation of isobutylene and/or tertiary butyl alcohol to methacrolein and then to methacrylic acid, there are other processes for production of methacrylic acid from the same feed stocks. One such prior art process, which will be referred to later, is the process disclosed by Escambia Chemical Corporation. Their patents show that isobutylene may be oxidized over a catalyst in the presence of nitric acid, preferably dinitrogen tetroxide, to form alpha hydroxy isobutyric acid. (U.S. 2,847,453 and 2,847,465), which is then dehydrated in the presence of a catalyst to form methacrylic acid (U.S. 2,881,545 and 3,562,230). 10
- 15 In the two-step process for oxidation of isobutylene and/or tertiary butyl alcohol to methacrylic acid, the effluent from the second oxidation step contains methacrylic acid and water as principal constituents, along with unreacted methacrolein and by-product acetic acid and impurities. The methacrylic acid typically will be a relatively small portion, less than 5 mol % of the total effluent stream, since substantial quantities of steam and inert gases are used in the process. For most uses, the methacrylic acid must be separated from the water, but recovery of methacrylic acid is difficult, since it forms an azeotrope with water. 15
- 20 One possible approach to obtaining essentially dry methacrylic acid would be to cool and condense the methacrolein oxidation reactor effluent to separate the inert gases from the methacrylic acid and water and then to distill the liquid mixture to obtain essentially dry methacrylic acid. Since water and methacrylic acid form an azeotrope containing about 23% by weight of the acid (at 760 mm Hg), it will be appreciated that such a distillation process will produce a substantial stream of methacrylic acid in water. Recycling such a stream to the oxidation step to recover the acid would be expected to result in losses of methacrylic acid to the lower acids. Consequently, a more efficient method of separation than simply distilling aqueous methacrylic acid would be preferred. 20
- 25 At least three other methods might be considered for the recovery of methacrylic acid from gaseous mixtures containing substantial amounts of water. The first such method is scrubbing of the methacrylic acid from the hot reactor effluent gas with solvents, while leaving the bulk of the water in the gaseous effluent. In the second and third methods, both the methacrylic acid and water are condensed and then treated with solvents to extract the acid from the water. In the second method, inorganic salts are introduced into a liquid mixture of solvent, acid and water in order to form a saltwater phase which can be easily separated and which contains little acid or solvent. In the third method, methacrylic acid is extracted with solvents from an acid-water mixture but without the use of salts to assist the separation. In both methods the water phase is drawn off and methacrylic acid is separated from the solvent and the residual water by azeotropic distillation. 25
- 30 The first process may be illustrated by U.S. Patent Nos. 3,926,744 issued to Noll et al., and 3,932,500 issued to Duembgen, et al., which relate to the recover of acrylic acid (rather than methacrylic acid) from water. In both patents, the effluent from the acrolein oxidation step is introduced into a scrubber while still in the vapor phase in order to selectively remove acrylic acid. 30
- 35 Duembgen scrubs the reactor effluent with extremely hydrophobic solvents, such as paraffin hydrocarbons, diphenyl and diphenyl ether under conditions which are established to minimize the amount of water removed from the gaseous stream. What water is removed is immediately stripped from the solvent-acid mixture in a desorbing column and returned to the scrubber. The stripped solvent-acid mixture is distilled to separate acrylic acid from the solvent. 35
- 40 Noll scrubs the hot reactor effluent gases in two steps with a mixture of solvent and water. The temperature in the first stage is kept relatively high and the quantities of solvent and water are adjusted to minimize the collection of water along with the acrylic acid. This permits distillation of acrylic acid directly from the solvent to produce acrylic acid. Noll suggests as solvents, monovalent aliphatic alcohols and the acetic acid esters or acrylic acid esters of such alcohols. 40
- 45 The second potential method of recovery of methacrylic acid, that is, by introducing inorganic salts for assisting in removal of water, may be illustrated by U.S. Patent No. 2,922,815, issued to Faerber, who disclosed the technique as used for recovery of acrylic acid (rather than methacrylic acid). Faerber mentions that metal salts have been used alone to separate water from acrylic acid and discloses a process which employs nickel salts along with a ketones (e.g. methyl ethyl ketone, methyl propyl ketone, methyl isopropyl ketone, diethyl ketone, ethyl isopropyl ketone and diisopropyl ketone) to carry out the separation of acrylic acid. The nickel salts form a salt-water layer which is substantially free of acrylic acid and which can be easily separated. Acrylic acid remains with the ketone-rich phase and may be separated by the subsequent 45
- 50 55 60 65

distillation. The introduction of nickel salts creates processing difficulties since they must be separated from the acrylic acid and any recycled streams. Avoiding the use of salts clearly would be preferred.

The third potential recovery method may be illustrated by U.S. Patent No. 3,896,153, issued to Ohru, et al. Ohru does not disclose a complete process for recovery of methacrylic or acrylic acids, but only discusses the optimization of a mixture of solvents consisting of methyl ethyl ketone and a xylene or ethyl benzene and shows that by optimizing the solvent composition, the distribution coefficient of the acid can be maximized. An aqueous solution of acid would be extracted by the optimized solvent system and the resulting acid-solvent mixture recovered by distillation or other conventional techniques.

Another example of the third method is given in U.S. Patent No. 3,414,485, issued to Speed. The patentee was particularly concerned with the preparation of methacrylic acid from a process previously mentioned, in which methacrylic acid is formed by catalytic dehydration of alpha hydroxy isobutyric acid. He states that the impurities carried over from the synthesis of methacrylic acid initiate polymerization of the methacrylic acid, and the azeotropic distillation was found to be inoperable due to excessive polymerization unless a preliminary extraction step was used. Polymerization was said to occur even if inhibitors were used. Consequently, it was found necessary to remove the troublesome impurities by extraction of crude methacrylic acid with a solvent. After condensing the dehydration reactor product to form a crude wet methacrylic acid, methacrylic acid was extracted with a solvent, e.g. xylene, toluene, n-octane, m-chlorobenzene, methyl amyl ketone, ligroin and methyl methacrylate. After settling, a water phase was separated from the acid-solvent mixture. Removal of polymerization initiators along with the water phase allowed Speed to use azeotropic distillation for recovery of the methacrylic acid from the solvent and any small amount of residual water.

In Japanese Kokai 71011/78, there is disclosed the extraction of methacrylic acid with methyl isobutyl ketone, which optionally includes a C₈-C₉ aromatic compound. It is stated that the optional C₈-C₉ aromatic compounds may be mixed in unlimited amounts with methyl isobutyl ketone.

It has been found that when methacrylic acid is formed via the oxidation of methacrolein, that fouling of equipment is a problem which is not necessarily eliminated by simply extracting crude methacrylic acid by solvents as suggested in the '485 patent. Further, since the recovery of by-product acetic acid is desirable, the solvents used for extraction of methacrylic acid must be selected to permit recovering acetic acid. A recovery process requiring employing a solvent extraction with specific solvents has been found to be useful, as will be described more fully hereafter.

In one aspect, the invention comprises a process for the recovery of methacrylic acid produced by the catalytic oxidation of methacrolein to methacrylic acid. The gaseous effluent from the oxidation reaction is cooled and methacrylic acid, by-product acetic acid, some unreacted methacrolein, water, and impurities are condensed and the condensate extracted with a mixture of solvents capable of separating methacrylic acid and by-product acetic acid from the bulk of the water present, while rejecting dissolved polymers or polymer precursors or catalysts from the solvent-methacrylic acid mixtures, thereby permitting operation of the recovery columns with substantially reduced fouling.

Selection of the solvent mixture is an important aspect of the invention. A mixed solvent consisting of a ketone selected from the group consisting of propanone, butanone, 2-pentanone, 3-pentanone, and mixtures thereof, plus an aromatic compound selected from the group consisting of benzene, toluene, and mixtures thereof, the relative proportions of the ketone and the aromatic being selected to reject dissolved polymers or polymer precursors or polymerization catalysts with the water phase, while permitting recovery of by-product acetic acid along with methacrylic acid during the distillation of rich solvent. Useful solvent mixtures will contain at least about 5 wt % of the aromatic compounds, although mixtures containing greater than 50 wt % of the aromatic compounds may be used. The solvent mixture most preferably is about 75 wt % methyl n-propyl ketone and about 25 wt % toluene.

In another aspect, the invention comprises a process for the recovery of methacrylic acid and acetic acid produced by the oxidation of isobutylene and/or tertiary butyl alcohol into methacrolein, followed by the recovery of methacrolein, and thereafter oxidation of the methacrolein to form methacrylic acid. The methacrylic acid and acetic acid are recovered by cooling and condensing the effluent from the second oxidation (of methacrolein) and then passing the condensed effluent into an extraction column where it is countercurrently contacted with a liquid solvent mixture selected according to the above criteria, preferably a methyl n-propyl ketone-toluene mixture, to recover methacrylic acid, acetic acid, and methacrolein. Substantially dry crude methacrylic acid including by-product acetic acid is obtained by distilling the extract and recovering the acids (methacrylic and acetic) as a bottoms product. Separation and recovery of methacrylic acid and acetic acid may be carried out in subsequent distillation facilities. Solvent is recovered as an overhead product during the separation of methacrylic acid and returned to the extraction column. Unreacted methacrolein is distilled from a portion of the recovered solvent in another column. Water is separated from the solvent as a water phase in the overhead facilities of the methacrylic acid recovery column and then stripped of its dissolved solvent in another recovery column.

In a preferred embodiment, the gaseous effluent is cooled and condensed by direct contact with a recirculating liquid stream comprising condensed effluent. A portion of the recirculating liquid stream is withdrawn and passed to an extraction column where it is countercurrently contacted with a solvent mixture selected according to the invention broadly, a mixture containing at least about 5 wt % of the aromatic compounds. A particularly preferred solvent contains about 75 wt % methyl n-propyl ketone and about 25 wt

% toluene. The bulk of the water is removed from the bottom of the extraction column and includes dissolved polymers and polymer precursors or catalysts. The solvent-methacrylic acid mixture is fractionated and the methacrylic acid and acetic acid are removed as bottoms product while the solvent and residual water pass overhead and are condensed and separated into two liquid layers. The solvent-rich layer 5 is returned to the extraction column, with a portion of the solvent-rich layer being fractionated to remove unreacted methacrolein. The water-rich layer is passed to a stripping column for removal of residual solvent. The bottom product from the solvent distillation is essentially dry methacrylic acid containing impurities and acetic acid, which can be separated in conventional facilities.

Figure 1 is a block diagram showing the two-step oxidation of isobutylene and/or tertiary butyl alcohol to 10 methacrylic acid and the recovery process of the invention.

Figure 2 shows the process for recovery of methacrylic acid and acetic acid from the effluent of the second oxidation step.

Figure 1 shows in a block diagram the two-step oxidation of isobutylene and/or tertiary butyl alcohol to methacrylic acid. Isobutylene and/or tertiary butyl alcohol are introduced, along with molecular oxygen, 15 which may be in the form of air, into a first oxidation step 10 for conversion to methacrolein in the presence of a suitable catalyst. Substantial quantities of water vapor, nitrogen, and carbon oxides typically are present in the reactor. They are shown in the diagram as being added to the oxidation step 10, however, depending upon the design selected, they may not necessarily be added as such. Nitrogen may enter with the oxygen supply and, if that is the case, nitrogen must be purged to maintain the desired amount in the oxidation 20 reaction. Large amounts of water are used and it may be added directly as steam or indirectly by adjusting the water content of the recycle gas stream. Water produced as a by-product of the reaction is disposed of during the product recovery process. The reaction typically is carried out at a temperature in the range of about 330-500°C, and at a pressure of up to about 14 kg/cm² gauge, over a catalyst typically comprising a mixture of base metal oxides. Since the reaction is highly exothermic, the catalyst is often placed inside 25 small diameter tubes and the heat of reaction removed by circulating a molten salt on the outside of the tubes.

Methacrolein is recovered and purified in recovery process 12 between the two oxidation steps, 10 and 14. Unreacted isobutylene separated during the recovery of methacrolein may be recycled to the first step oxidation as shown in the diagram, along with carbon oxides and other inerts.

30 After recovery, the methacrolein may be fed to the second oxidation step 14 where the methacrolein is oxidized by molecular oxygen to methacrylic acid in the presence of substantial amounts of water vapor carbon oxides and nitrogen at temperatures typically in the range of 270-450°C and at pressures up to about 7 kg/cm² gauge, over a mixed base metal oxide catalyst. The comments made previously with regard to the direct introduction of steam and inerts apply to this second oxidation step also. That is, they may be added 35 as such, but need not necessarily be, depending upon the design selected.

The present invention is particularly concerned with improvement in the recovery of methacrylic acid from the second oxidation step 14, and more particularly, with the recovery of by-product acetic acid along with the methacrylic acid. The recovery process is shown generally in Figure 1 to consist of a cooling and condensing step 16, including separation of gases for recycle to the second oxidation stage and followed 40 immediately by recovery of the crude methacrylic acid by extraction with a suitable solvent and then separation from the solvent 18 and followed by purification of the crude methacrylic acid 19. The recovery process 18 is shown in more detail in Figure 2.

The cooling and condensing of hot effluent gases from the second oxidation step may be carried out as shown in Figure 2, although alternative means will occur to those skilled in the art. In the embodiment of 45 Figure 2, the effluent typically leaves the second (methacrolein) oxidation step 14 via line 20 at a temperature of about 290-325°C and a pressure of about 0.25 kg/cm² gauge. It may be passed through indirect heat exchange 22 to cool the effluent gases and to recover the reaction heat, such as by generating steam. Leaving heat exchange 22, the temperature would typically be about 150°C upstream of the subsequent quenching step 24, at which temperature the effluent stream remains in the gaseous form. Alternatively, if 50 no intermediate cooling is used, the gases enter the quench facilitates at the temperature of the reactor outlet. As will be seen later, compared to use of only a ketone solvent, the use of a mixture containing an aromatic compound is coincident with an increase in polymer in the extraction column. The mode of quenching the reactor effluent gases has been found to effect the formation of polymer in the subsequent solvent extraction column. The preferred techniques for such quenching are not a part of the present 55 invention, but are disclosed and claimed in another U.S. patent application. A recirculating liquid stream for direct contact quenching of the gases is derived by cooling and partially condensing the gases to a suitable temperature, say about 40°C. The two major constituents, that is, methacrylic acid and water are accompanied by unreacted methacrolein, by-product acetic acid and impurities. Two types of direct contacting may be provided. The recirculating liquid may contact the gases in line 20 as well as in quench 60 tower 26. Heat is removed by direct contact with the liquid quench streams and water, methacrylic acid and acetic acid are condensed along with smaller amounts of impurities. The heat acquired by the quench stream is removed by indirect heat exchange in exchanger 30, which will ordinarily employ cooling water or air at ambient temperature. The liquid leaving the quench tower 26 is recirculated through exchanger 30 and returned to the tower 26 via line 28 or sent via line 29 to contact the incoming hot gases in line 20. The 65 temperature of the recirculating streams may be selected to optimize the recovery of methacrylic acid, while

minimizing the size and operating costs of the equipment involved. Gases exiting the quench tower 26 are returned via line 34 to the second oxidation step (14 in Figure 1) in order to avoid losses of valuable materials such as methacrolein carried overhead from the quench tower 26. Quench tower 26 is provided with suitable means for contacting the upwardly flowing effluent gases with the liquid quench stream, such as packing of various types and gas-liquid contacting trays which are familiar to those skilled in the art.

The net production of methacrylic acid, acetic acid, and water, along with unreacted methacrolein and impurities such as acrylic acid, is passed via line 36 to the extraction column 38. Column 38 is provided with suitable means for contacting the countercurrent liquid streams circulating within the column and may employ packing, trays and the like for this purpose. The column is operated at near atmospheric pressure and in the presence of a suitable solvent. In general, for efficient recovery of methacrylic acid the solvents will have a boiling point lower than that of methacrylic acid and will form an azeotrope with water capable of being efficiently condensed by ambient temperature coolants. Since acetic acid is to be recovered as a by-product, the solvent also must not carry acetic acid overhead. Generally, suitable solvents will have the ability to extract methacrylic acid, acetic acid, methacrolein almost completely into the solvent, while leaving troublesome impurities in the water withdrawn from the bottom of the extraction column 38. It has been found that by proper selection of a solvent the appearance of solids, which are generally polymers and which foul the distillation columns and their reboilers, is minimized and by-product acetic acid can be recovered along with the methacrylic acid.

In particular, it has been found that ketones and particularly the pentanones appear to be the solvents of choice with regard to the separation of the methacrylic acid and acetic acids from water. Though the pentanones would be presumed interchangeable, straight chain ketones are found substantially superior to branched chain ketones, since much more solids appear when branched chain ketones are used. Further, it has been discovered that the use of even the best straight-chain ketone, methyl n-propyl ketone, is unexpectedly unsatisfactory. Although the distribution coefficients are very favorable for the separation of methacrylic and acetic acids from water, fouling of the reboilers in down-stream distillation towers has been found to be alleviated when aromatics, especially toluene, are combined with straight-chain ketones in particular proportions. It is believed that suitable combinations of solvents, such as the preferred mixture of methyl n-propyl ketone and toluene do not extract dissolved polymers, polymer precursors, and/or polymerization catalysts and thus such undesirable materials are left in the water phase, which is withdrawn from the bottom of the extraction column 38. If such materials are withdrawn with the water phase, fouling in down-stream columns is minimized. Unfortunately, addition of aromatics unfavorably lowers the distribution coefficients of methacrylic and acetic acids so that losses of these desirable products into the water phase are increased. Consequently, it has been found necessary to add only so much aromatics as will remove the source of fouling, while retaining the ability of the ketone to extract the desired methacrylic and acetic acids. The aromatics are also associated with the appearance of a different type of polymer in the extraction column. For example, while the use of methyl n-propyl ketone is associated with only traces of polymer in the extraction column is very large when only toluene is used. It has been found that the larger the amount of aromatic compound, the more important it becomes to quench the gases properly.

The solvent enters the bottom of the column 38 after being cooled to a suitable low temperature, typically about 25°C, in heat exchanger 37.

The solvent has a lower density than the liquid product of the quench tower 26 and thus the solvent passes upward through column 38 countercurrently to the quenched liquid and extracts the products to be recovered, that is, methacrylic and acetic acids, along with unreacted methacrolein, and leaving water and the troublesome impurities to be withdrawn from the bottom of column 38 via line 46. The impurities which are removed by the mixed solvents according to the invention are believed to be polymers or polymer precursors or polymerization catalysts which result in the appearance of solids deposition in downstream columns.

Although the conditions are very favorable to the desired separation, nevertheless some residual solvent is present in the water withdrawn via line 46 and some residual water is present in the rich solvent leaving the extraction column 38 via line 39. The rich solvent passes to solvent stripper 40 where the methacrylic and acetic acids are separated by distillation. Vapor and liquid streams required to carry out the separation are generated by reboiler 41 and condenser 43, respectively. Essentially solvent-free methacrylic and acetic acids are withdrawn via line 42 and sent to another fractionating column for separation (block 19 in Figure 1). Vapor from the top of the column 40 is condensed in condenser 43 and two liquid phases form in separator 44, a water-rich phase 45b containing a minor amount of dissolved solvent and a solvent-rich phase 45a containing a minor amount of dissolved water. The separator 44 is designed to permit the two phases to separate and to be withdrawn for further processing or re-use. The water-rich phase is sent to solvent recovery column 48, along with the bulk of the water separated in column 38. The combined streams (46 and 47) enter the top of column 48 and as the liquid passes downwardly over the trays (or packing and the like) residual solvent is stripped out by vapor generated by reboiler 49. Essentially solvent-free water is removed from the bottom of column 48 and disposed of or reused as desired. Solvent vapor containing an equilibrium amount of water vapor passes overhead via line 50 and is returned to the overhead vapor line from the solvent stripper 40 and is condensed in condenser 43 and collected in separator 44. The solvent-rich phase in separator 44 is returned to column 40 as reflux 51a as necessary to carry out the separation between the solvent and the methacrylic and acetic acids. The remaining solvent is sent to column 38 via stream 51b to

repeat the extraction process. It should be noted that if more than the minimum amount of aromatic compound needed to reject dissolved polymers, polymer precursors, or catalysts from the solvent -- methacrylic acid mixtures is employed losses of acetic acid will tend to increase. Consequently, it may become necessary to recover acetic acid rejected into the water stream.

- 5 Inasmuch as any unreacted methacrolein present in the quenched liquid from column 26 passes overhead in the solvent stripper 38 and is found in the solvent-rich phase 45a, the methacrolein will tend to concentrate in the solvent stream circulating through the extraction column 38 and solvent stripper 40. In order to remove the methacrolein, a purge stream may be taken from the solvent-rich phase 45a, either intermittently or continuously. This stream (51c) could be disposed of or, optionally, could be recovered in a distillation column, such as that designated 52 in Figure 2. Solvent essentially free of methacrolein is withdrawn from the bottom of column 52 via line 58 for recycle to column 38 while methacrolein is recovered overhead in column 52 and returned to the second stage oxidation via line 55. Water and methacrolein pass overhead from column 52 and after being condensed in condenser 52, are collected in separator 54. A portion of the condensate is returned as reflux via line 56 to column 52 and the net recovery of methacrolein is returned to the second stage oxidation. Heat is supplied to column 52 by reboiler 57. As with the other columns previously described, column 52 could be provided with packing, trays, or other suitable internal means for contacting gases and liquids. 5
- 10 It will be understood by those skilled in the art that inhibitors, such as hydroquinone and others are commonly used to prevent polymerization of the aldehydes and acids during the recovery process.
- 20 As previously mentioned, selection of a solvent has been found to be critical in avoiding the presence of polymers in the various recovery columns and/or their reboilers. More specifically, a mixed solvent is used combining a straight chain ketone having three to five carbon atoms is mixed with a minor amount of an aromatic, namely, benzene and/or toluene. Experiments have shown that the pentanones are particularly good solvents since the distribution coefficients (the ratio between the concentration in the solvent phase and the water phase) are highly favorable to the desired separation between water and methacrylic acid. However, it has been found that while methyl isopropyl ketone and methyl n-propyl ketone have similar ability to extract methacrylic acid and acetic acid, they differ significantly in their effect on the degree of fouling of towers and reboilers by solid polymers. Also, addition of toluene to methyl n-propyl ketone has been found to greatly reduce the appearance of solid polymers, although at the expense of reduced distribution coefficients for the desired products and thus, higher costs for the extraction step and perhaps, additional facilities to recover acetic acid from water. Since the toluene employed also effects the appearance of polymer in the extraction step, it is preferred that the amount of toluene used be minimized, say as low as 5 wt % toluene in methyl n-propyl ketone. The use of higher concentrations of toluene are preferred, particularly 25 wt % toluene, but concentrations above 50 wt % may be used if desired. 10
- 30 The following examples illustrate the effects of the preferred solvents, which have been discussed generally above. 25
- 35 30
- 55

Example 1

- 40 Liquid from the quench step containing 27.8 wt % methacrylic acid, 3.5 wt % acetic acid, 62.5 wt % water, and small amounts of unreacted methacrolein and impurities is mixed with various solvents and stirred for one hour, then settled for at least two hours and separated. The solvent layer from the extraction, which is rich in methacrylic acid and acetic acid is batch distilled in a 1" diameter, 15 plate Oldershaw column. The column reboiler is maintained at about 120°C and a reflux ratio of 2 to 1 is employed. Hydroquinone is included at 1000 ppm (wt) based on the original charge. Air is sparged into the reboiler at a rate of about 1.5% of the vapor flow in the column. Where possible to do so, the distillation was continued until about 30% of the feed material remained in the bottom of the column. The results are shown in Table 1 which shows that, although they provide favorable distribution coefficients, both methyl isopropyl ketone and methyl n-propyl ketone are likely to cause fouling problems in the distillation of the solvent rich in methacrylic acid, acetic acid and methacrolein. It is believed that the polymer formed during the distillation is polymethacrylic acid and, that the polymerization is promoted by the presence of a compound which can be removed with the water phase from the extraction step. Whether or not this explanation is correct, the results show that addition of toluene has the effect of reducing the solids formation and that when 25 wt % toluene is added to methyl n-propyl ketone a batch distillation for eight hours produced no solids at the temperature of distillation. 40
- 50 Since the addition of toluene causes an undesirable lowering of the distribution coefficients of methacrylic acid, acetic acid, the methacrolein, the mixture of methyl n-propyl ketone and toluene is a less attractive extraction solvent. The unexpected benefits of the addition of toluene however make its use, or alternatively, of benzene, an important factor in making practicable the solvent extraction distillation process for recovery of methacrylic acid, while retaining the by-product acetic acid with the principal product. 45
- 55 50
- 55

TABLE 1

5	Solvents	Solvent/Quench Liquid wt/wt	Distribution Coefficient for Methacrylic Acid	Time Distilled Hrs.	Observations	5
10	MIPK (methyl isopropyl ketone)	0.75	11.7	4	Solids appeared after two hours, severe polymeriza- tion terminated run	10
15	MNPK (methyl n-propyl ketone)	0.75	10.7	4+	Solids appeared after four hours and increased rapidly causing termination of run	15
20	90% MNPK + 10% toluene	0.75	10.6	8	Solids observed during dis- tillation, and substantial amount appeared on cooling the apparatus	20
25	75% MNPK + 25% toluene	0.75	10.3	8	No solids observed during distillation, but minor amounts appeared during cooling of the column after distillation was completed.	25

Example 2

A continuous extraction-distillation apparatus is constructed for extraction of the quenched product of methacrolein oxidation, using a 1" diameter York-Scheibel column having 11 stages each mixed by an agitator and separated by 3" long packed sections. The quenched feed containing 38.5 wt % methacrylic acid, 4.6 wt % acetic acid, 51.6 wt % water, and small amounts of methacrolein and impurities is fed into the top of the column and passes downwardly countercurrent to a mixture of 75 wt % MNPK and 25 wt % toluene entering at the bottom of the column. The solvent to water mol ratio is 0.5. The column is operated at a constant temperature of about 25°C.

It is found that the extract (rich solvent) withdrawn from the top of the column contains essentially all of the methacrylic acid and 95-98% of the acetic acid and methacrolein. The raffinate (stripped feed) withdrawn from the bottom of the column consists of about 90 mol % water and contains a small amount of acetic acid and impurities. The extract is fed continuously to a 2" diameter Oldershaw column having 50 trays to separate the mixed solvent from the crude methacrylic acid-acetic acid mixture. An essentially complete separation is obtained with reflux ratios of 0.65 and 1.26.

After successful operation with the solvent mixture of 75 wt % MNPK/25 wt % toluene the use of a mixture of 75 wt % MIPK/25 wt % toluene is begun. Within a few minutes the Oldershaw Column is plugged with a reddish solid, believed to be a polymer of methacrylic acid.

As can be seen from the above Example 2, the results obtained with MNPK are satisfactory, while unexpectedly, the chemically related MIPK cannot be used. The reason for the difference in performance between the two pentanones is not known. However, it appears that straight chain ketones may be used, but that branched chain ketones are clearly inferior.

The following example will illustrate the effect of changing solvent composition on the appearance of polymer in the extraction column. It will be seen that, while addition of an aromatic compound such as toluene is effective to reduce polymer in the distillation of extract solutions, the use of aromatics has an adverse effect on the extraction operation.

Example 3

The effluent gases from the second-stage reactor are sent directly to a quench column similar to column 26 in Figure 2, but without the use of the preliminary in-line contacting shown in this figure. The gases entered the quench column at a temperature of about 200-250°C and were cooled to a temperature of about 40-45°C by contact on distillation trays with a recirculating liquid having a composition equal to that of the condensed liquid product.

The data of Table II show that when methyl n-propyl ketone is used to extract methacrylate acid and acetic acid from the condensed liquid, that very little solids appeared in the extraction column, but that when toluene is used as an extractant, a large amount of solids appear. Neither of these single solvents is preferred for use as an extractant since they either do not extract acetic acid satisfactorily (toluene) or they are associated with the appearance of solids in downstream distillation columns (MNPK). According to the present invention, at least about 5 wt % toluene in methyl n-propyl ketone should be used for the extraction, but mixed solvents containing more than 50 wt % of the aromatic component could be used. The mixture of

about 75 wt % methyl n-propyl ketone and about 25 wt % toluene is particularly preferred since such mixed solvents have been shown to help to minimize the appearance of solids, while satisfactorily extracting both methacrylic and acetic acids.

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TABLE II

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10 Solvent	Inhibitor	Solids found in Extraction Column	10
MNPK	1000 ppm hydroquinone	trace	
15 75 wt % MNPK 25 wt % toluene	1000 ppm hydroquinone	~ 1500 ppm	15
20 Toluene	1000 ppm hydroquinone	high	20

In a commonly assigned patent application, it is shown that the amount of solids which appear in the extraction column 38 are substantially reduced when the line 20 carrying hot gases is heated by a jacket and insulated to prevent condensation of the gases until they reach the quench column, where they can contact recirculating liquid containing an inhibitor. In addition, use of a rapid in-line quench such as is indicated in Figure 2 further reduces the amount of the solids in the extraction column, thus permitting additional flexibility in selecting the mixture of solvents.

In a specific example of the process of the invention according to Figure 2, an effluent from the second oxidation step is cooled by indirect heat exchange 22 to a temperature of about 150°C and thereafter cooled further by direct contact with recirculating liquid streams (28 and 29) of condensed effluent so that the recycled gases leaving the top of column 26 are at a temperature of about 40°C. The recycle gas stream contains principally nitrogen, water vapor, unreacted methacrolein, and minor amounts of by-products and impurities. The recirculating quench streams 28 and 29 and the slip stream 36 sent to column 38, each contain about 13.9 mol % methacrylic acid, about 81.9 mol % water, about 3.1 mol % acetic acid, about 0.1 mol % of other impurities expressed as acrylic acid, and about 1 mol % methacrolein. About 1000 mols/hr of condensate are fed to extraction tower 38 via line 36. About 666 mols/hr are withdrawn from the bottom of the column via line 46, which includes 658 mols/hr of water, along with about 8 mols/hr of methyl n-propyl ketone. The column operates at atmospheric pressure and a temperature of about 25°C. The overhead stream (line 39) contains about 740 mols/hr of a mixture of methyl n-propyl ketone, toluene, methacrylic acid, acetic acid, and water typically about 225 mol/hr ketone, 73 mol/hr toluene, 139 mol/hr methacrylic acid, 31 mol/hr acetic acid, and 217 mol/hr water. The overhead stream (39) passes to the solvent stripper 40 where the solvent is removed and 171 mol/hr of crude methacrylic acid containing 139 mol/hr of methacrylic acid and 31 mol/hr of acetic acid is produced. The net production of solvent is contained in a stream containing 233 mol/hr methyl n-propyl ketone, 73 mol/hr toluene, 45.6 mol/hr of water, and 54.5 mol/hr of methacrolein. Of this solvent 319 mol/hr are returned to the extraction column 38 via 51b, and 77 mol/hr are sent via 51c to the methacrolein recovery column 52. The reflux 51a to column 40 is 1000 mol/hr. The column 40 is operated below atmospheric pressure, say at about 200 mm Hg. absolute in order to minimize column temperatures. The water-rich layer, 45b, which is sent to the stripping column 48, contains approximately 99.2 mol % water and 0.8 mol % methyl n-propyl ketone and in this example has a rate of about 195 mol/hr. The stream 47 joins stream 46 which contains the bulk of the water removed from the methacrylic acid in the extraction column 38 and the combined stream is stripped in column 48. After stripping, about 829 mol/hr of water will be removed from the bottom of the stripping column 48 at a temperature determined by the column pressure, while all of the ketone fed to column 48 (about 9.6 mol/hr) will be removed as an overhead product along with about 22 mol/hr of water and returned via line 50 to the overhead vapor line from column 40. The water stripping column 48 will be operated at a suitable pressure which will permit return of the overhead vapors to the solvent stripping column 40. The stripped water from the bottom of the column may be reused or disposed of. However, in the event that solvent mixtures rich in toluene are used (which are less effective in extraction of acetic acid) recovery of acetic acid from the stripped water may be economically justified.

A purge stream may be removed from the reflux to the solvent stripping column 40 (line 51c in Figure 2). The flow rate of the purge stream will be adjusted so that it contains an amount of methacrolein equivalent to that entering the methacrylic acid recovery system, or about 10 mol/hr in this example. It will carry with it an equilibrium amount of solvent and water from separator 44 (about 44 mol/hr ketone, 14 mol/hr toluene, and 9 mol/hr water in this example). The methacrolein recovery column 52 may be operated at essentially

atmospheric pressure. About 63 mol/hr of solvent-water mixture containing about 68.5 mol % methyl n-propyl ketone is returned to the extraction column 38 via line 58. After condensation of the overhead vapor in exchanger 53 and cooling to about 40°C, the methacrolein is collected in separator 54 and is withdrawn for return to the second oxidation step.

- 5 The foregoing description of the preferred embodiments of the invention is intended for illustration only and should not be considered as limiting the scope of the invention, which is defined by claims which follow. 5

CLAIMS

- 10 1. A process for the recovery of methacrylic acid and acetic acid from the effluent vapors of the vapor phase catalytic oxidation of methacrolein to methacrylic acid in the presence of molecular oxygen, water vapor, and inert gases; the process comprising 10
 - (a) cooling and condensing said effluent to a predetermined temperature and thereby forming a vapor portion comprising substantially unreacted methacrolein, oxygen, water vapor, and inert gases and a liquid portion comprising substantially methacrylic acid, acetic acid, water, a minor amount of unreacted methacrolein, and impurities; 15
 - (b) separating said liquid portion of (a) from said vapor portion of (a);
 - (c) extracting the methacrylic acid, acetic acid, and methacrolein from said liquid portion of (a) with a mixed solvent consisting essentially of at least one ketone selected from the group consisting of propanone, butanone, 2-pentanone, and 3-pentanone, and at least one aromatic compound selected from the group consisting of benzene and toluene, and recovering the solvent after said extraction, thereby separating the water content of said liquid portion; and 20
 - (d) distilling the solvent recovered from said extraction to separate said solvent from the extracted methacrylic acid, acetic acid, and methacrolein.
- 25 2. The process of claim 1 wherein said extraction solvent is a mixture of at least about 5 wt % of said aromatic compounds. 25
3. The process of claim 1 wherein said extraction solvent is a mixture of about 75 wt % methyl n-propyl ketone and about 25 wt % toluene.
4. The process of claim 1, claim 2 or claim 3 wherein said cooling and condensing of (a) comprises the steps of (i) cooling said oxidation effluent and thereafter (ii) quenching said cooled effluent of (i) by directly 30
 contacting said effluent with a liquid stream comprising condensed effluent, and (iii) withdrawing a liquid portion of the condensed effluent stream of (ii) equivalent in quantity to said liquid portion (a). 30
5. The process of any one of claims 1 to 4 wherein said methacrolein is prepared by catalytic oxidation of isobutylene and/or tertiary butyl alcohol.
- 35 6. A process for the preparation of methacrylic acid comprising: 35
 - (a) in a first oxidation step, oxidizing in the presence of a catalyst a gaseous feed stream containing isobutylene or t-butyl alcohol or mixtures thereof and molecular oxygen, water vapor, and inert gases to for methacrolein;
 - (b) recovering the methacrolein from the effluent gases of said first oxidation step of (a);
 - 40 (c) in a second oxidation step, oxidizing in the presence of a catalyst the recovered methacrolein of (b) in a gas phase reaction in the presence of molecular oxygen, water vapor, and inert gases to form methacrylic acid; 40
 - (d) cooling, and condensing the effluent gases from the second oxidation step of (c) by directly contacting said effluent gases with a liquid stream comprising condensed effluent;
 - 45 (e) withdrawing a portion of the condensed liquid stream of (d) containing substantially all of the methacrylic acid and acetic acid formed in (c) water, a minor amount of unreacted methacrolein, and impurities; 45
 - (f) extracting the methacrylic acid, acetic acid, and methacrolein from said liquid portion of (e) with a mixed solvent consisting essentially of at least one ketone selected from the group consisting of propanone, butanone, 2-pentanone, and 3-pentanone, and at least one aromatic compound selected from the group consisting of benzene and toluene, and recovering the solvent after said extraction, thereby separating the water content of said liquid portion of (e); and
 - 50 (g) distilling the solvent removed from said extraction to separate said solvent from the extracted methacrylic acid, acetic acid, and methacrolein. 50
- 55 7. The process of claim 6 wherein said extraction solvent is a mixture containing at least about 5 wt % of said aromatic compounds. 55
8. The process of claim 6 wherein said extraction solvent is a mixture of about 75 wt % methyl n-propyl ketone and about 25 wt % toluene.
9. A process as claimed in claim 1 or claim 6, substantially as hereinbefore described with particular reference to the Examples. 60
- 60 10. A process as claimed in claim 1 or claim 6, substantially as illustrated in Figure 1 or Figure 2 of the accompanying drawings.

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11. A process as claimed in claim 1 or claim 6, substantially as illustrated in any one of the Examples.
 12. Methacrylic acid when obtained by the process claimed in any one of the preceding claims.

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